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REPORT

CD NO.

50X1-HUM

COUNTRY USSR

DATE OF  
INFORMATION 1949SUBJECT Scientific Chemicals, organophosphorus  
compounds

DATE DIST. 3 Aug 1951

HOW  
PUBLISHED Monthly periodicalWHERE  
PUBLISHED Moscow/Leningrad

NO. OF PAGES 7

DATE  
PUBLISHED Feb 1951SUPPLEMENT TO  
REPORT NO.

LANGUAGE Russian

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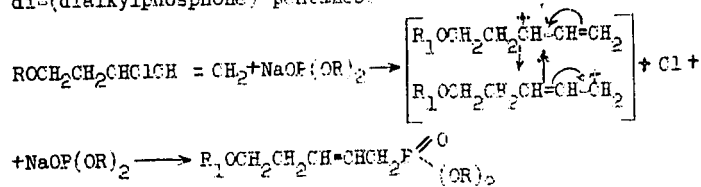
SOURCE Zhurnal Obshchey Khimii, Vol XXI, No 2, 1951, pp 382-388.

THE ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO UNSATURATED COMPOUNDS:1. THE ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO  $\beta,\beta$ -DIMETHYL VINYL KETONE

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[Phosphonic acid esters synthesized by the reaction described  
in this paper can be easily converted into halophosphonates, i.e.,  
compounds which are known to have cholinesterase inhibitor activity.  
This refers to a potentiality only: there is no information to the  
effect that the Russian investigators are actually pursuing a line  
of research aimed at the synthesis of cholinesterase inhibitors  
under application of the reaction described.]

In one of the preceding investigations [1] we studied the action of di-  
alkylphosphorous acids on halogen-containing allyl isomers. It was shown that  
in this reaction not only esters of alkoxy ethyl allyl phosphonic acid are  
formed, according to the normal scheme for primary haloid allyl compounds and  
for secondary ones with complete allyl rearrangement, but also there occurs an  
addition to them of sodium dialkylphosphonic acid with the formation of alkoxy-  
di-(dialkylphosphone) pentanes.

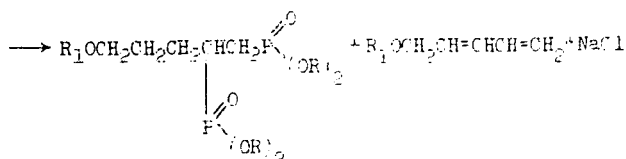
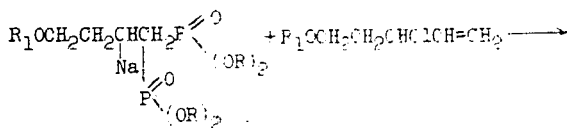
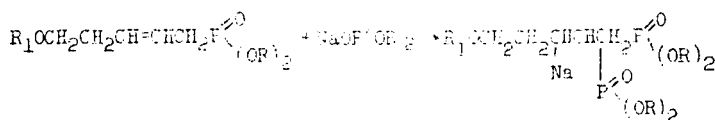


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Since the above case of addition of sodium salts of dialkylphosphorous acids to unsaturated compounds is, up to now, the only one known in literature and is of great theoretical interest, we decided to investigate this new type of reaction more closely, using as an example unsaturated compounds belonging to various groups of organic compounds.

The present report describes results obtained in the study of the reaction of the addition of unsaturated dialkylphosphorous acids to  $\beta, \beta$ -dimethyl vinyl ketone, belonging to the class of unsaturated ketones. As the investigations of I. N. Nazarov and his associates showed, divinyl ketones are extremely reactive compounds. Thus, he succeeded in adding to  $\beta, \beta$ -dimethyl vinyl ketone water, alcohols, amines, diene hydrocarbons, malonic and acetoacetic esters, furane derivatives, hydrogen chloride, and hydrogen sulfide [2]. The addition reactions have selective character: the majority of the compounds are added to the unsubstituted vinyl group, while some, such as hydrogen chloride and hydrogen sulfide, on the other hand, are added primarily to the substituted vinyl group.

We conducted the experiments on the addition of dialkylphosphorous acids to  $\beta, \beta$ -dimethyl vinyl ketone under various conditions. In the first experiments, a solution of sodium dialkylphosphite in dialkylphosphorous acid was added to the ketone. The reaction was very violent, and the yields of the addition products were very small and these products highly unstable. Later it was established that better results are obtained by the addition of a small quantity of an alcoholic solution of sodium alcoholate to the mixture of ketone and dialkylphosphorous acid, as was the case in a series of experiments conducted by I. N. Nazarov and his associates. By this method, the reproducibility of the experiments and the yields of products were fully satisfactory. The addition to  $\beta, \beta$ -dimethyl divinyl ketone of dimethyl phosphorous, diethyl phosphorous, diisobutyl phosphorous and dibutyl phosphorous acids was studied. The addition of dimethyl- and of diethyl phosphorous acid proceeds most energetically because the temperature of the reaction mixture after the addition to the mixture of a few drops of alcoholic solution of alcoholate is raised to 80°-90°C, and the reaction practically runs its course within a few minutes. The addition of higher dialkyl phosphorous acids proceeds less energetically and requires a considerably greater quantity of sodium alcoholate.

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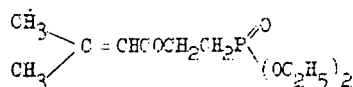
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The constants and the yields of the products of the addition are shown in the table below:

No	Formula	Bp	Mol Re- fraction $n_D^{20}$	Density $d_4^{20}$	Yield in %
1	$(CH_3)_2C=CHCOCH_2CH_2P(=O)(CH_3)_2$	169°-171°C at 1 mm	1.4711	1.1130	59
2	$(CH_3)_2C=CHCOCH_2CH_2P(=O)(OC_2H_5)_2$	149°C at 1 mm	1.4660	1.0658	52
3	$(CH_3)_2C=CHCOCH_2CH_2P(=O)(OC_4H_9)_2$	188°-190°C at 10 mm	1.4511	1.0013	48.5
4	$(CH_3)_2C=CHCOCH_2CH_2P(=O)(OC_4H_9)_2$	at 198°-200°C	1.4623	1.0111	57

For determination of the structure of the products obtained, the product of the addition of diethylphosphonic acid to  $\beta, \beta$ -dimethyl divinyl ketone was subjected to detailed investigation. Titration of the product with a bromine solution showed that it contained only one double bond. On saponification of the product with hydrochloric acid, ethyl chloride was obtained, in a quantity corresponding to the theoretical computation based on the assumption of the presence of one diethyl phosphonic radical in the molecule. The presence in the product of one diethyl radical was also confirmed by the titration which resulted in the saponification of the phosphonic acid with a solution of caustic alkali. No phosphoric acid was detected in the saponification products, while it should have been formed if the phosphorus of the phosphonic radical in the addition product had been attached to the carbon atom in the  $\alpha$  position to the ketone group [3]. (Action of phenyl hydrazine on the acid gave a crystalline product with a melting point of 143°-144°C; the product resulting from the addition of phenyl hydrazine to phosphoric acid melts at 155°-156°C under effervescence; a mixed sample of both products melted at 130°C). Finally, on oxidation of the product with potassium permanganate, a large quantity of acetone whose semicarbazone melted at 176°C was obtained. The presence of the ketone radical in the product investigated was shown by color reactions with sodium nitroprusside and  $\beta$ -naphthol and sulfuric acid and the isolation of liquid phenyl hydrazine which distilled over at 210°C at 2 mm. The data obtained indicate that the product of the addition of diethyl phosphorous acid to  $\beta, \beta$ -dimethyl divinyl ketone has the following formula:

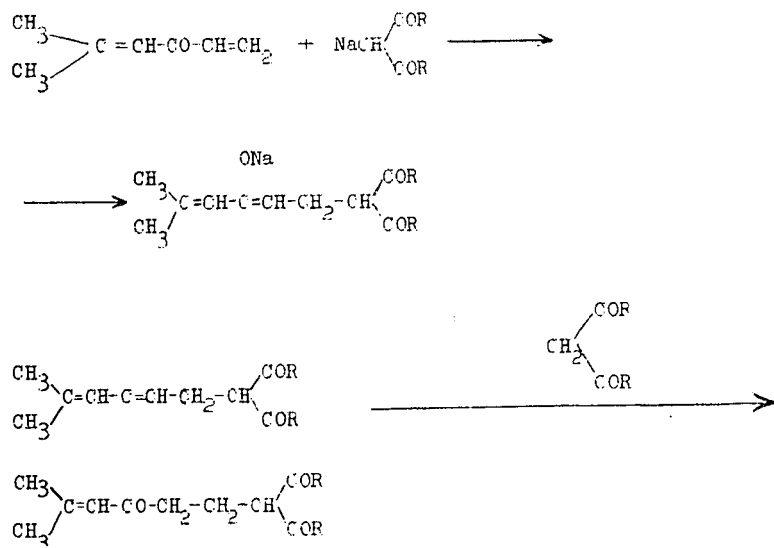


As far as the mechanism of the reaction investigated by us is concerned, we believe it possible to express the following ideas: I. N. Nazarov and L. Terexkova assume that the addition of malonic and acetoacetic esters and of acetyl acetone to  $\beta, \beta$ -dimethyl vinyl ketone takes place after the formation of the corresponding sodium derivatives, with their subsequent addition in the 1 and 4 positions to the unsaturated ketone, according to the following scheme:

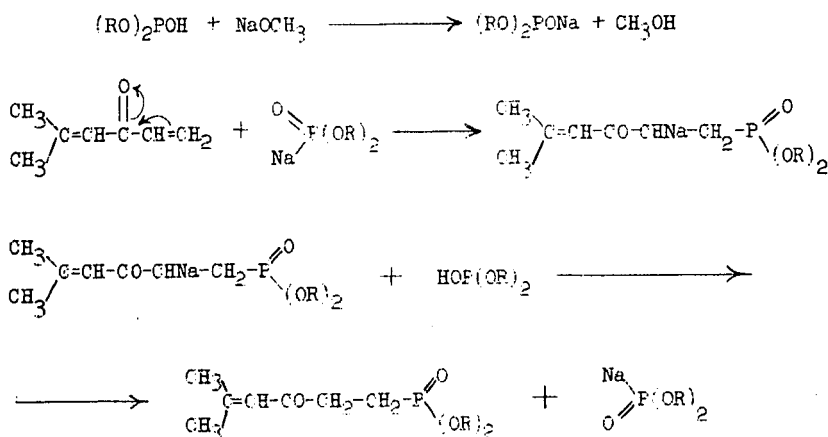
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However, as it has been shown by our experiments that dialkyl phosphorous acids are added not only to unsaturated ketones, but also to unsaturated phosphonic ethers where the above scheme (addition in the 1, 4 position) cannot be applied, it must be considered likely that addition takes place directly in the 1, 2 position, as follows:



## EXPERIMENTAL PART

Addition of Diethyl Phosphorous Acid to  $\beta,\beta$ -dimethyl Divinyl Ketone.  
Experiment 1

In 14 g of diethyl phosphorous acid a piece of metallic sodium the size of a pinhead was dissolved. The solution obtained was then added drop by drop to 11 g of  $\beta,\beta$ -dimethyl divinyl ketone. The reaction generates a large amount of heat and the mixture becomes very hot. To reduce the temperature of the reaction, the mixture was cooled with cold water during the entire period of the drop-by-drop addition of the diethyl phosphorous acid.

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After addition of the entire quantity of the diethyl phosphorous acid, the mixture was heated on a water bath for 3 hours and then distilled in vacuum from an Arbuzov flask. From the yield of the first distillation, 13 g of a fraction with the boiling-point range of 159°-165°C at 5 mm were separated. About 10 g of clear, extremely viscous yellow colored liquid remained in the flask. Attempts to distill it under 2-mm pressure were unsuccessful.

Under intensive heating, decomposition took place, accompanied by formation of large quantities of white fumes. Analysis of this residue showed a content of 13% of phosphorus, while the product of the addition of two molecules of diethyl phosphorous acid to  $\beta, \beta$ -dimethyl divinyl ketone should contain 16.1%. The fraction distilling in the boiling range of 159°-165°C at 5 mm, on repeated distillation, boiled in the main at 149°C at 2 mm.

$n_D^{20}$  1.0658  $n_D^{20}$  1.4660

0.1704 g of material. 38.7 ml NaOH (T=0.0200). Found: 12.2% P.

$C_{12}H_{21}O_4P$ . Calculated: 12.5% P

In the second experiment, the reaction was carried out in an ether solution. The results remained as before. In a series of analogously conducted reactions, a considerably smaller quantity of the addition product was obtained. Generally, only a nondistilling product, mentioned above, was formed.

#### Experiment 2

To the reaction mixture made from 14 g of diethyl phosphorous acid and 11 g of  $\beta, \beta$ -dimethyl divinyl ketone, about ten drops of a saturated alcohol solution of sodium ethylate were added slowly from a dropping funnel under cooling with cold water. The reaction proceeds very violently, with strong heating of the reaction mixture. Further addition of sodium ethylate no longer affected the heating of the reaction mixture. After 2 hours of heating over a water bath, the mixture was transferred to an Arbuzov flask and distilled in vacuum. Fourteen grams of a product with a boiling point of 176°-180°C at 11 mm,  $n_D^{20}$  of 1.4658 were obtained. The residue weighed 8.7 g.

#### Investigation of the Product With Bp 149°C at 2 mm

The product is liquid, fairly viscous, slightly yellow in color, soluble in water and in various organic solvents.

#### Titration with Bromine

Quantitative determination of double bonds in the product was carried out by the method of McIlhenny (approximation from the Russian). 0.4050 g of substance: hyposulfite used (for addition): 36.3 ml (T=0.017008). Bromine reacting: 0.30 g. Calculated P, 0.27 g.

#### Saponification

Six grams of product and 30 ml of dilute (1:1) hydrochloric acid were heated for 10 min in a sealed tube at 170°-180°C. After unsealing the tube, the ethyl chloride was evaporated. Its last traces were removed from the material by heating the tube in warm water. The difference in weight of the tube before and after the removal of the ethyl chloride was 3.3 g. Theoretically, according to the calculation, 3.1 g of ethyl chloride should be liberated per one phosphonic radical. The aqueous solution, after removal of the ethyl chloride,

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was evaporated many times in a porcelain dish with distilled water. After removal of all the hydrogen chloride, the water was driven off under vacuum. The residue yielded phosphonic acid in the form of a viscous liquid. It was left in a dessicator over sulfuric acid for a month. Crystallization was not observed. A total of 4.8 g of acid was obtained.

From 6 g of phosphonic ester, the yield should have been 4.7 g. Four and two-tenths of acid were dissolved in water and titrated with a solution of caustic. Calculated on the basis of the total acid (4.7 g) the quantity of NaOH should have been 1.98 g, but actually was 2.15 g. Six-tenths g of phenyl hydrazine were added to 0.6 g of acid which, weighed in a small porcelain dish, and diluted with 5 ml of ethyl alcohol. Within several minutes, a large quantity of precipitate was formed. It was filtered and dried. A total of 0.75 g of crystalline substance was obtained. After two recrystallizations from alcohol, the substance melted at  $143^{\circ}\text{--}144^{\circ}\text{C}$  without effervescence. The product of the combination of phenyl hydrazine with phosphoric acid melts at  $155^{\circ}\text{--}156^{\circ}\text{C}$  with strong effervescence. A mixed sample of both products melted at  $130^{\circ}\text{C}$ .

#### Oxidation

A total of 2.8 g of the product was dissolved in 200 ml of water. Then, 3.8 g of potassium permanganate, ground to a powder, were added gradually, with constant shaking and cooling by running water. After standing one day over the manganese dioxide, the solution bleached. The entire mass was transferred to a flask and 15 ml of it were distilled off. The distillate had the characteristic odor of acetone. Semicarbazide was added to it, and the mixture was then allowed to stand for a day. Ten min after the semicarbazide had been added, the precipitation of semicarbazone had already begun. A total of 0.3 g of acetone semicarbazone with a boiling point of  $176^{\circ}\text{C}$  was obtained. After the manganese dioxide had been filtered off, the aqueous solution was evaporated almost to dryness, the salts were decomposed by the addition of sulfuric acid, and the free acids extracted with ether. After removal of the ether by distillation, the residue was distilled from a small flask under vacuum. It yielded fractions whose boiling points were not established.

#### The Action of Phenyl Hydrazine

A total of 5 ml of absolute ethyl alcohol and 1.5 g of free phenyl hydrazine were added to 3 g of the addition product. The reaction mixture was allowed to stand at room temperature, and then in the cold for 15 days. Crystallization did not take place. About 2 g of phenyl hydrazone with a boiling point of  $210^{\circ}\text{C}$  at 2 mm were separated from the product of the vacuum distillation of the mixture. The phenyl hydrazone had the consistency of a very thick oil.

0.2858 of substance. 54.5 ml NaOH used. Found: 9.15, 8.9% P.  
 $\text{C}_{17}\text{H}_{27}\text{O}_3\text{N}_2\text{P}$ . Calculated: 9.20% P.

#### Addition of Dimethyl Phosphorous Acid to $\beta,\beta$ -dimethyl Divinyl Ketone

To a mixture of 11 g of  $\beta,\beta$ -dimethyl divinyl ketone and 11 g of dimethyl phosphorous acid, several drops of a saturated alcohol solution of sodium ethylate were added slowly from a dropping funnel under cooling. After the addition of each drop, strong heating of the mixture was observed. A total of ten drops was required for completion of the reaction. The reaction mixture was vacuum-distilled after heating for 3 hours in a water bath. After two redistillations, 13 g of product with a boiling point of  $169^{\circ}\text{--}171^{\circ}\text{C}$  at 13 mm were separated.

$d_4^{20}$  1.1130;  $n_D^{20}$  1.4711

0.1204 g of substance, 31.2 ml NaOH ( $T=0.02000$ ) used. 0.2026 g of substance, 50.6 ml NaOH used. Found: 14.3, 13.8% P.  $\text{C}_9\text{H}_{17}\text{O}_4\text{P}$ . Calculated: 14.1% P.

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Addition of Diisobutyl Phosphorous Acid to  $\beta,\beta$ -dimethyl Divinyl Ketone

To the mixture, consisting of 8 g of  $\beta,\beta$ -dimethyl divinyl ketone and 14 g of diisobutyl phosphorous acid, a solution of sodium ethylate was added drop by drop under water cooling. A much larger quantity of sodium ethylate was required for the completion of the reaction than for the reactions of the addition of dimethyl and ethyl phosphorous acids. A total of 10.7 g of product was obtained after distillation of the mixture.

Bp  $188^{\circ}$ - $190^{\circ}$ C at 10 mm,  $d_4^{20}$  1.0013,  $d_D^{20}$  1.4511. 0.1629 g of substance, 30.2 ml NaOH ( $T=0.0200$ ) used. 0.1589 g of substance, 29.7 ml of NaOH used. Found: 10.2, 10.3% P. Calculated: 10.2% P.

Addition of Dibutyl Phosphorous Acid to  $\beta,\beta$ -dimethyl Divinyl Ketone

The reaction was carried out with 10 g of ketone and 18 g of dibutyl phosphorous acid in the presence of sodium ethylate, by the method described in the above experiments. Sixteen grams of product were obtained by distilling the mixture.

Bp  $198^{\circ}$ - $200^{\circ}$ C at 12 mm,  $d_4^{20}$  1.0111,  $n_D^{20}$  1.4623. 0.1536 g of substance, 27 ml of NaOH ( $T=0.02034$ ) used. Found: 9.96% P.  $C_{15}H_{29}O_4P$ . Calculated: 10.20% P.

## SUMMARY

It is shown that dialkyl phosphorous acids, in the presence of small quantities of alcoholates of alkali metals, easily combine with  $\beta,\beta$ -dimethyl divinyl ketone with the formation of the corresponding esters of phosphonic acids. The structure of the products obtained is shown and a mechanism of their formation is proposed.

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